Thermocatalytic H_2-Production via Oxygen-Free Methane Aromatization

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Start Date = May 2004
Planned Completion = 2006

CERC
Clean Energy Research Center

Research Goals and Objectives

- Portable or Stationary H_2 Production
- Local feed stream
- No Green-house gas by products
- High selectivity and turnover
- Easy separation of by-products
- Biomass compatible

Relevance to Current State-of-the-Art

- Steam-methane reformation produces about 95% of the hydrogen used in the United States.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

Ni catalyst

- Thermocatalytic cracking of methane (R&D stages)

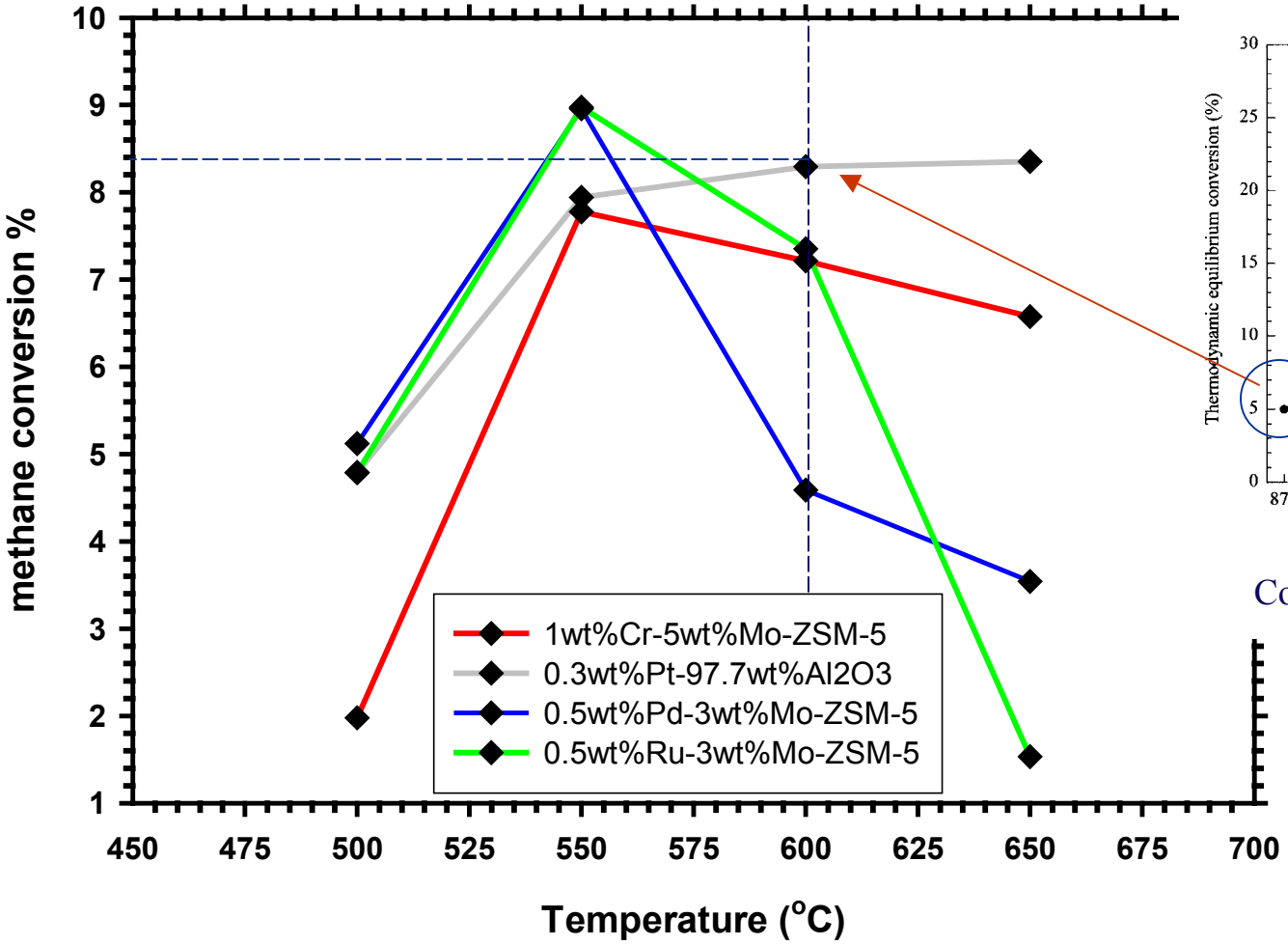
$$6CH_4 \xrightarrow{Mo/ZSM-5} C_6H_6 + 9H_2$$

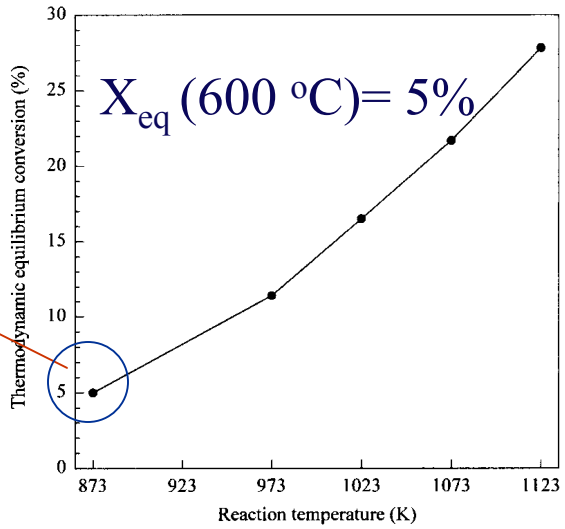
No trace CO from reformed hydrogen!

Relevance to NASA

- UHP H_2 is produced, no separation processes needed
- Very clean with minimal environmental consequences
- No green house gasses, biomass compatible
- Important to NASA's space launch activities.
- Creation of high technology job opportunities
- Cost effective

FTIR conversion (based on methane peak area)





Correlation between thermodynamic equilibrium conversion and reaction temperature*

G.H.S.V.=434/hr^{-1}

Surpassed Thermodynamic Equilibrium Conversion!

* Y. Zhang et al. J. Natural Gas Chem., 12(2003)145

Budget, Schedule and Deliverables

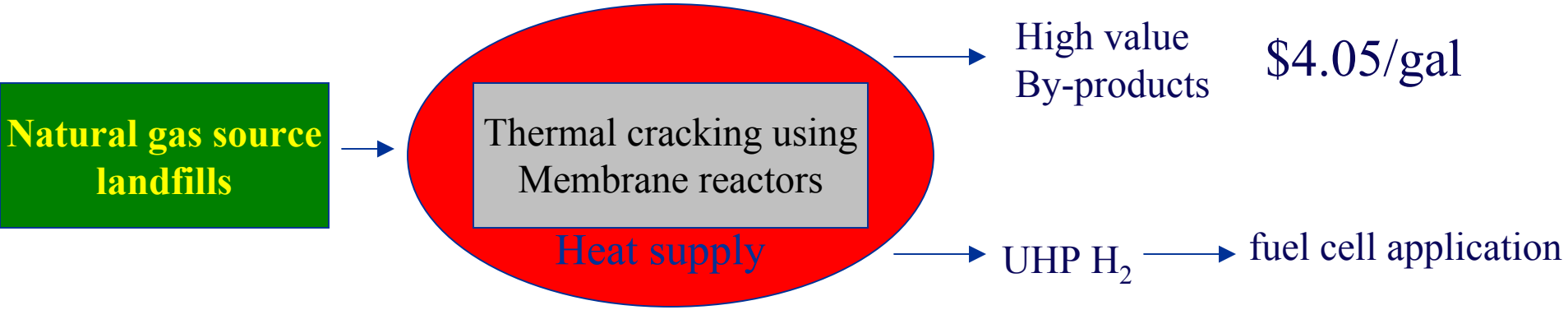
Schedule	Deliverables	Budget*
May 2004	Start Literature Review	$ 2,440.00
Jun. 2004	Equipment ordered	$ 15,200.00
Aug. 2004	Setup is ready (FTIR studies)	$ 2,880.00
Sep. 2004	Catalyst prepared 3-5wt%Mo-ZSM-5	$ 2,440.00
Oct. 2004-May 2005	Test different promoted catalyst systems Metal ions used: Ru,Pd,Cu,Co,Cr,Pt	$ 14,640.00
April 2005	H_2 conversion studies using GC	$ 2,440.00
May 2005-Aug. 2005	Reactor upgrade: 5 Micron Pd coating Literature review	$ 8,320.00
Aug. 2005- Oct 2005	Optimize reactor parameters (reaction T and P)	$ 4,320.00
Oct 2005-??	Test new catalyst systems and pretreatments	

***Includes student stipend and tuition**

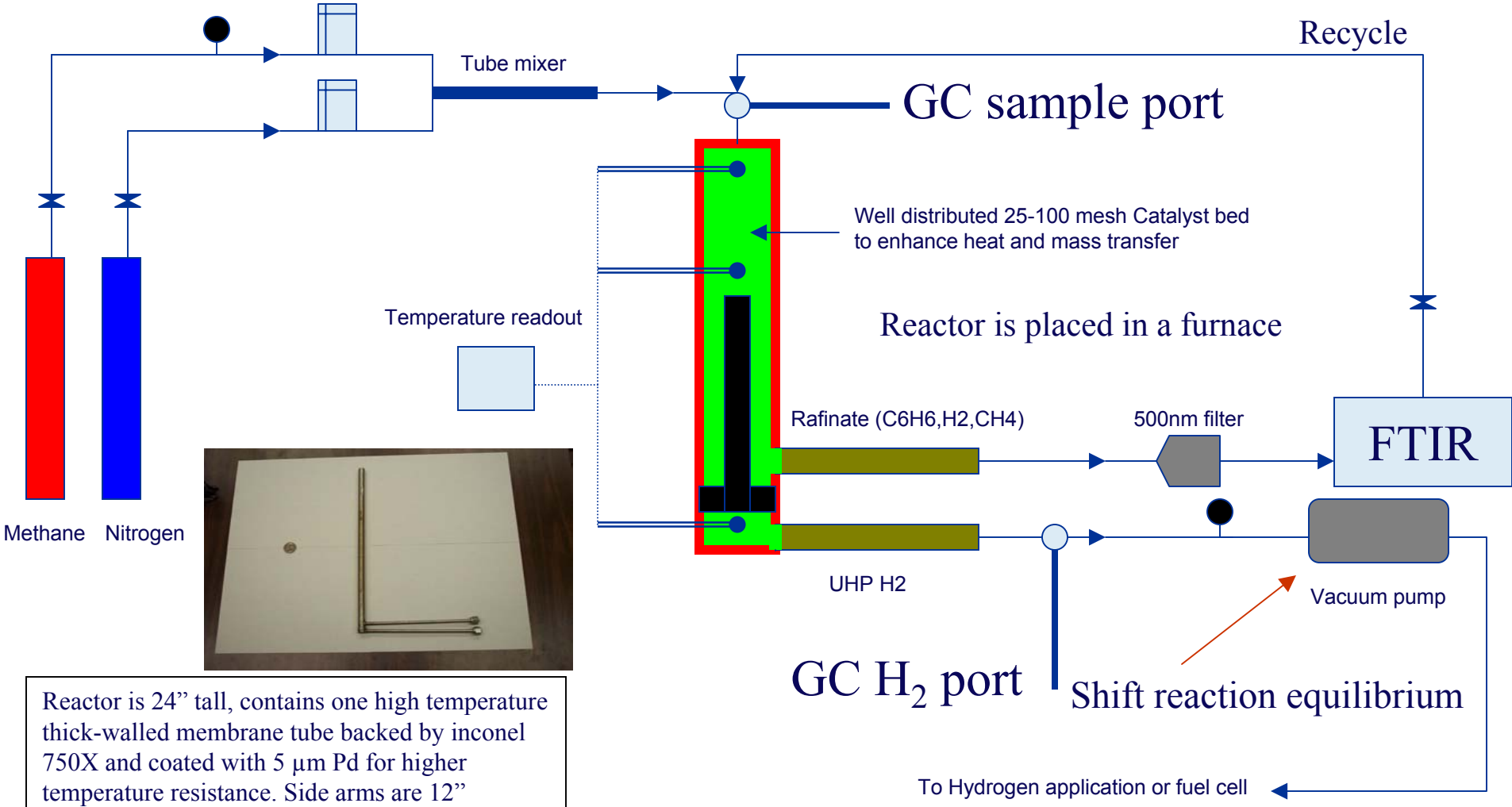
Anticipated Technology End Use

- Membrane reactors produce UHP H_2 → fuel cell applications.
- The global benzene market is expected to grow by approximately 5 million tonnes between 2005 and 2008.

Shell Oil: World Phenol/Acetone Conference 2005.

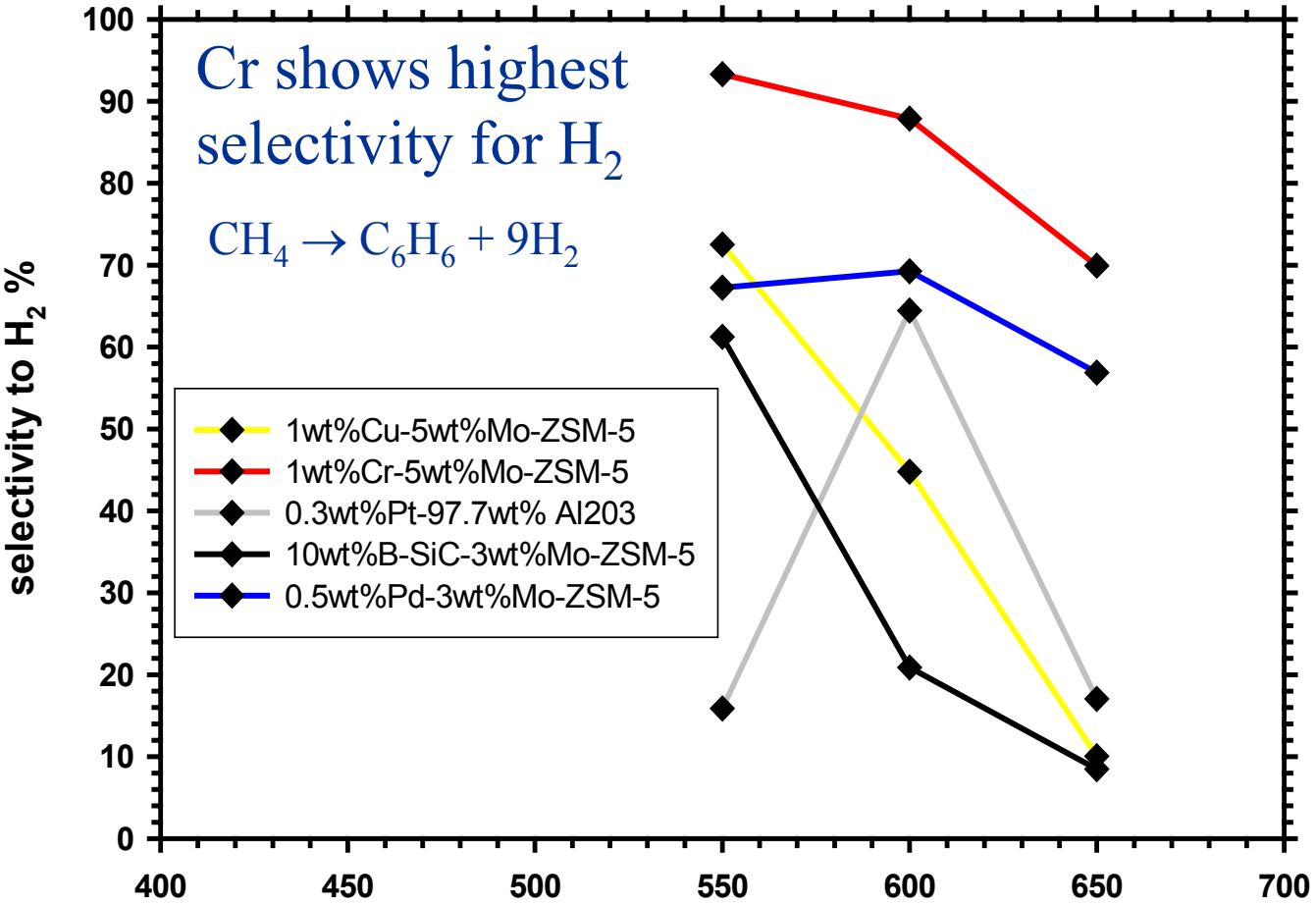


Accomplishments and Results: Methane membrane reactor block diagram



Reactor is 24” tall, contains one high temperature thick-walled membrane tube backed by inconel 750X and coated with 5 µm Pd for higher temperature resistance. Side arms are 12” stainless steel

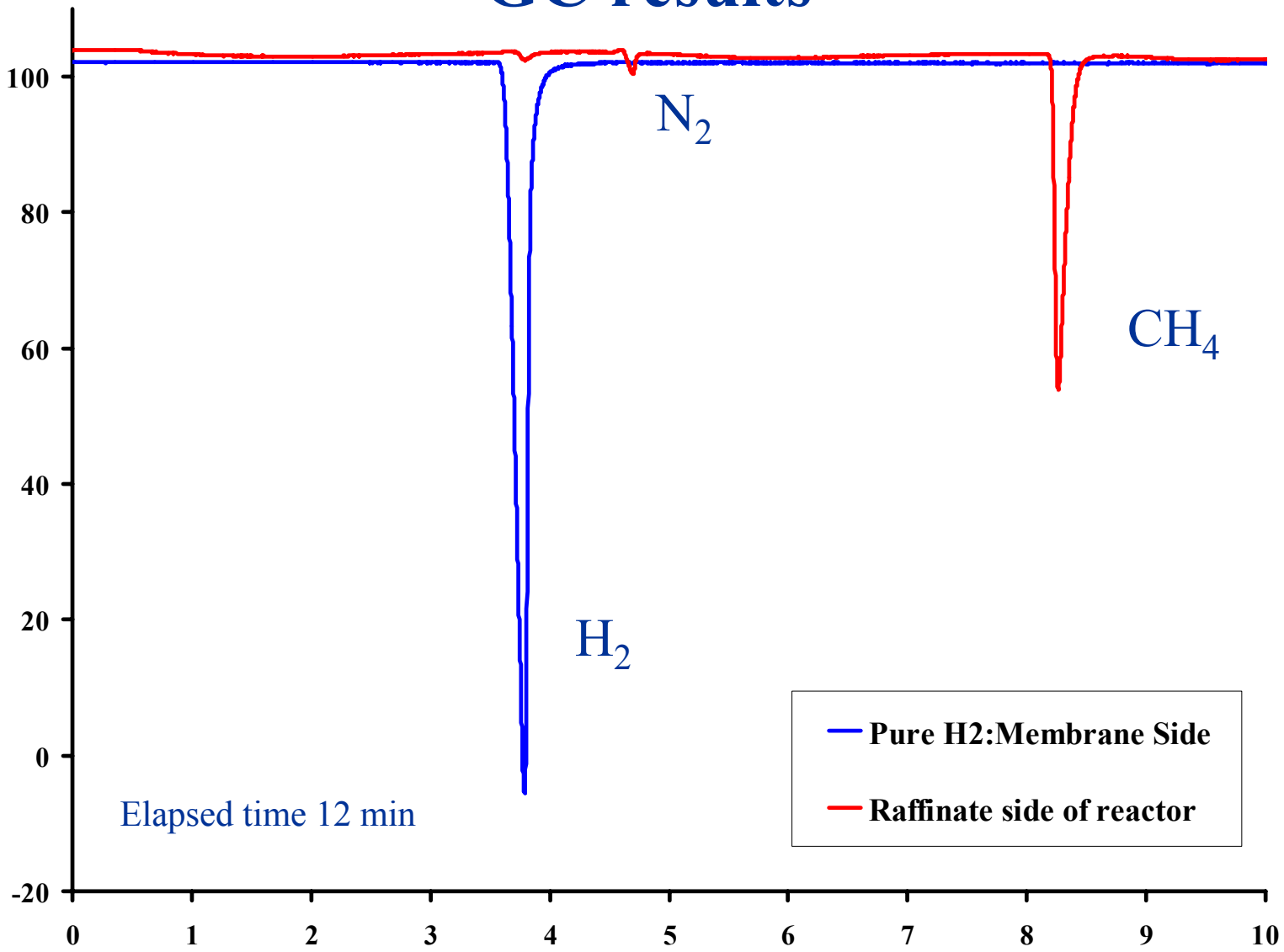
GC selectivity results (based on peak area)



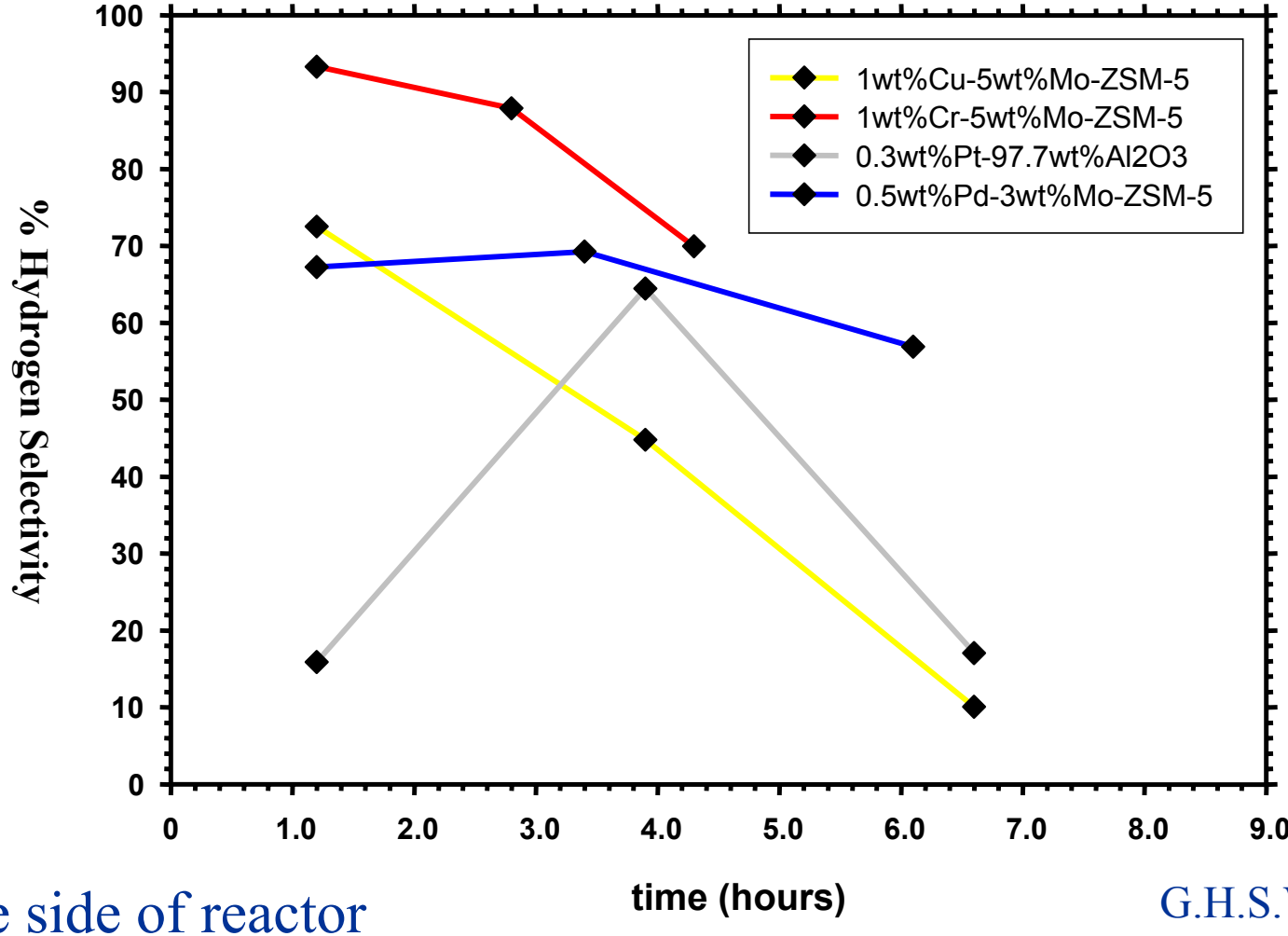
Membrane side of reactor

G.H.S.V.=434/hr^{-1}

GC results


100
80
60
40
20
0
-20
0
1
2
3
4
5
6
7
8
9
10
N_2
H_2
CH_4
Elapsed time 12 min
Pure H2:Membrane Side
Raffinate side of reactor

GC H_2 Selectivity vs. Time



Membrane side of reactor

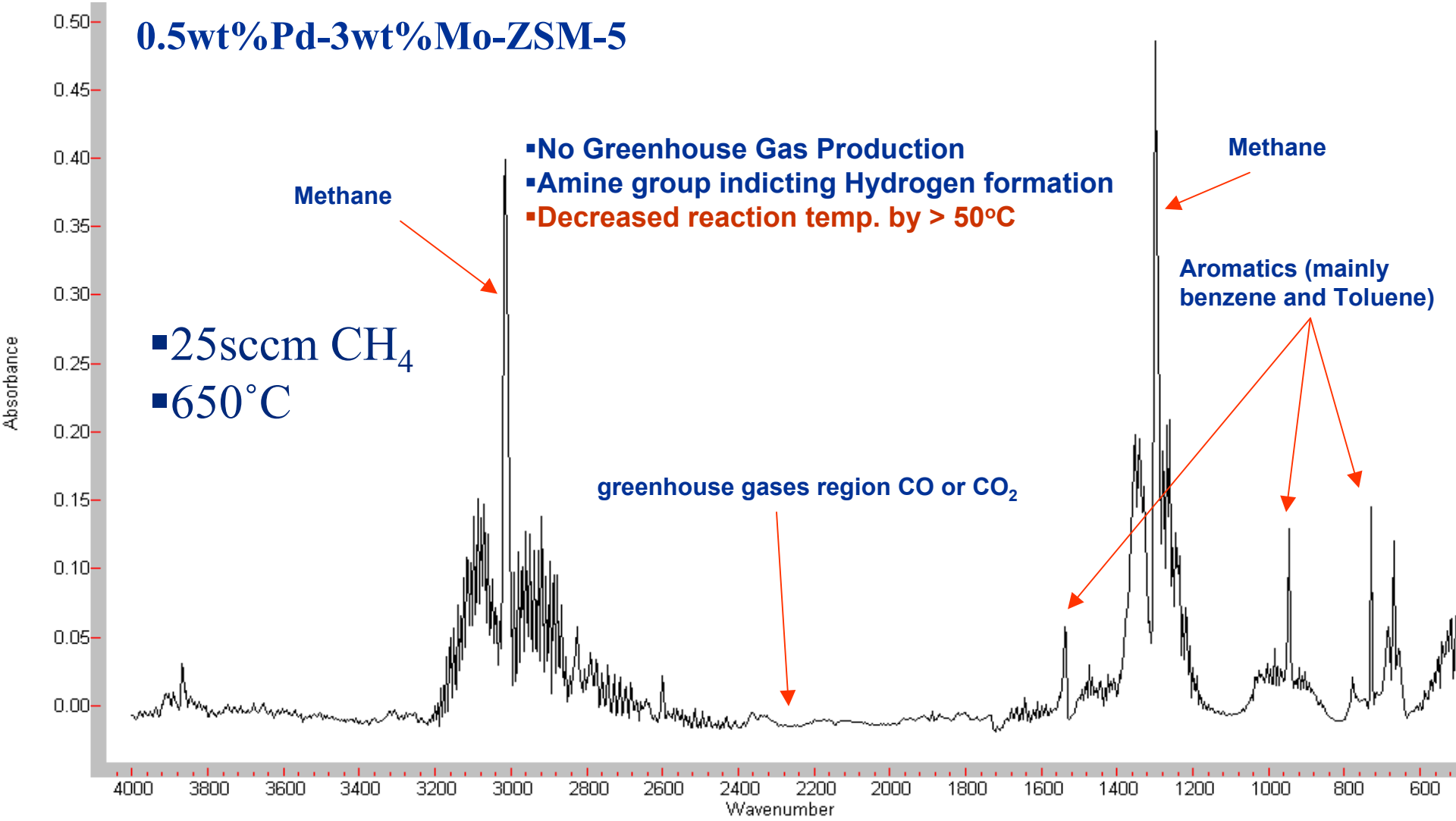
G.H.S.V.=434/hr-1

Catalyst systems prepared

Catalyst formula	Objective
Mo/ZSM-5	original & reference
10wt% β-SiC-3wt%Mo/ZSM-5	Improved temperature distribution and heat conduction
(Pd,Ru)-3wt%Mo/ZSM-5 (bimetallic)	improving conversion and stability
(Co, Cu , Cr,)-3-5wt%Mo/ZSM-5 (bimetallic) and Pt/Al_2O_3	Optimization and H-selectivity

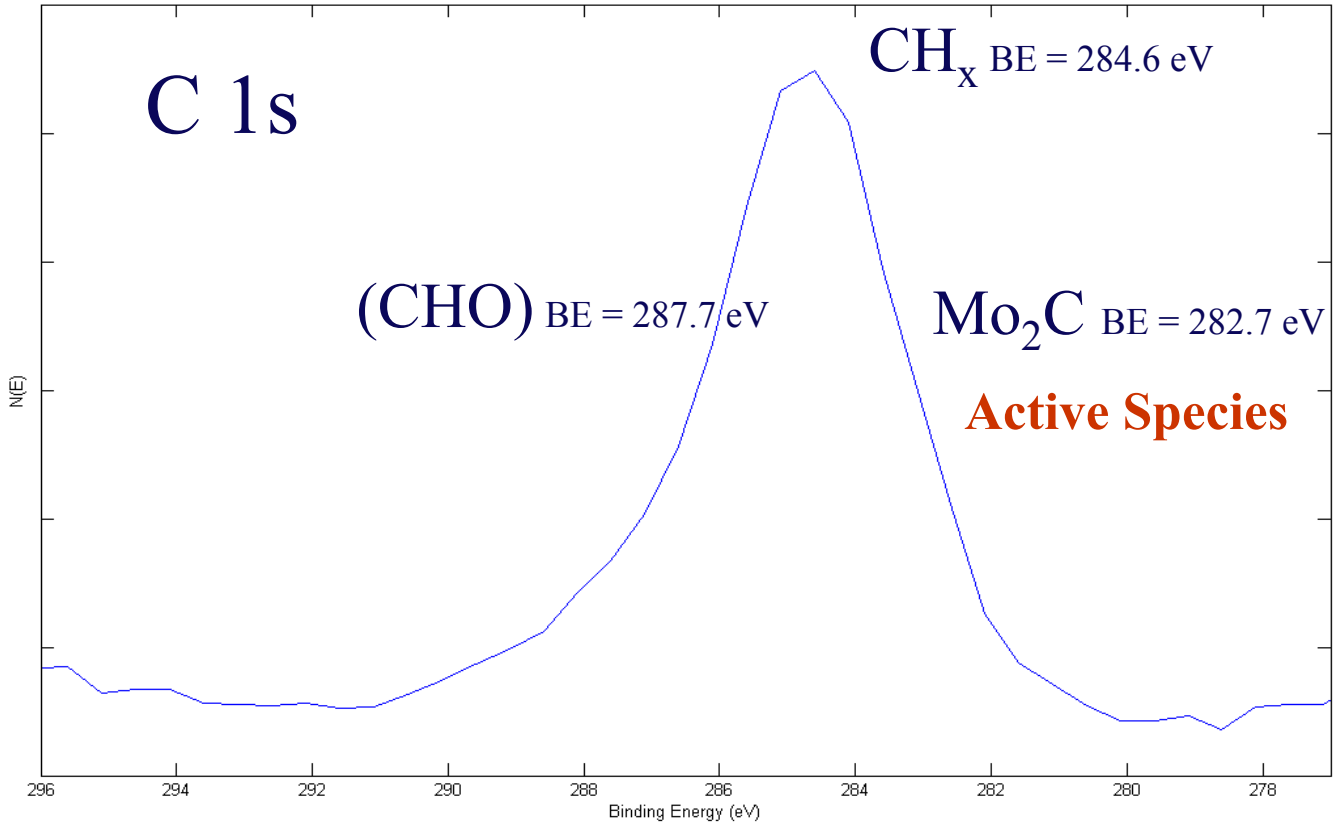
Prepared by incipient wetness co-impregnation of the ammonium form of the zeolite

Fourier Transform Infrared Absorbance Spectrum

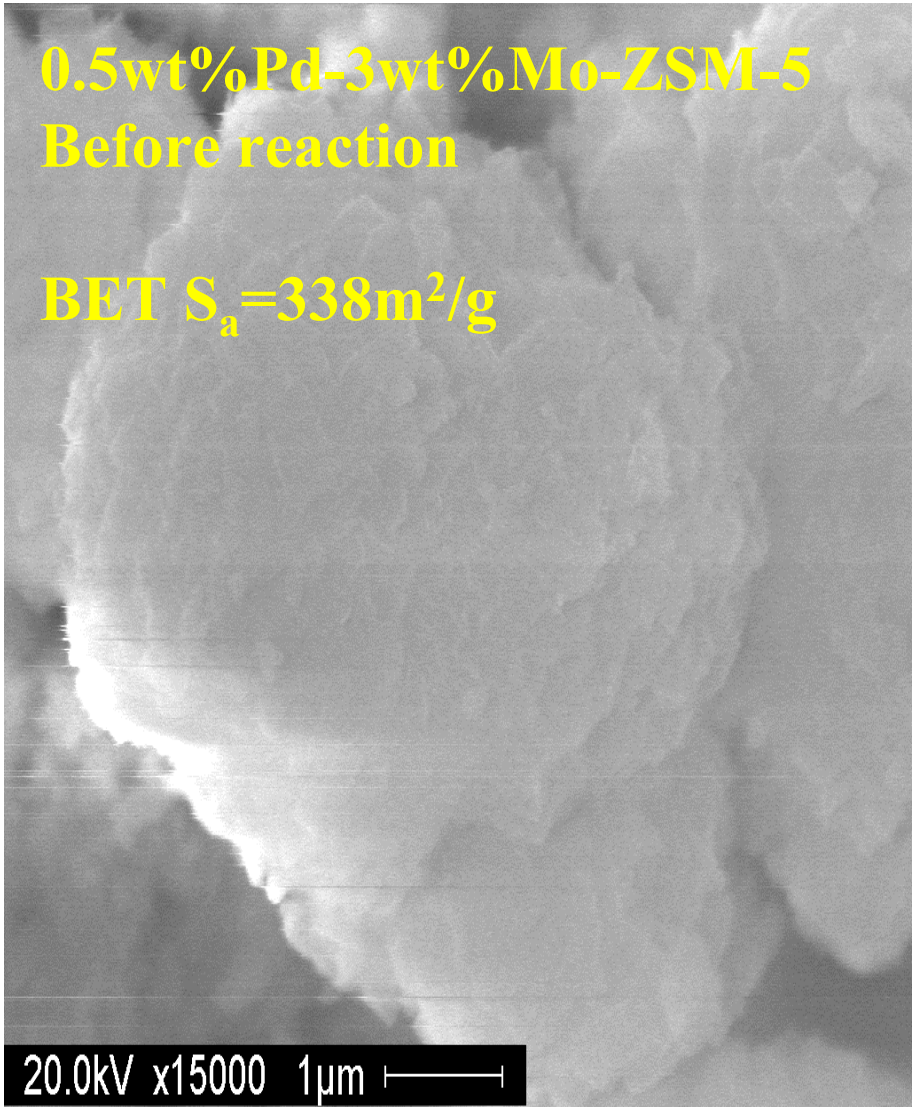


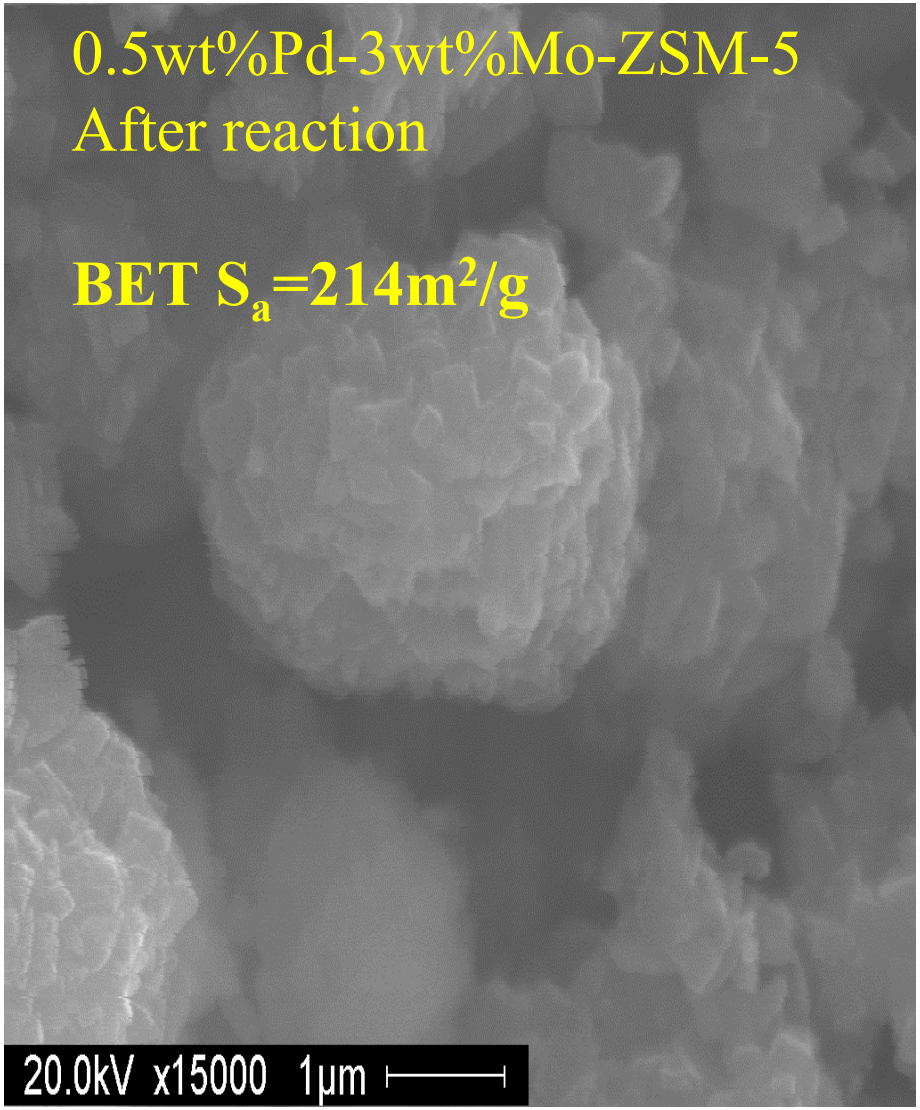
X-ray Photoelectron Characterization

Heavy carbonaceous deposits present a major obstacle for a better understanding of the reaction process and development.

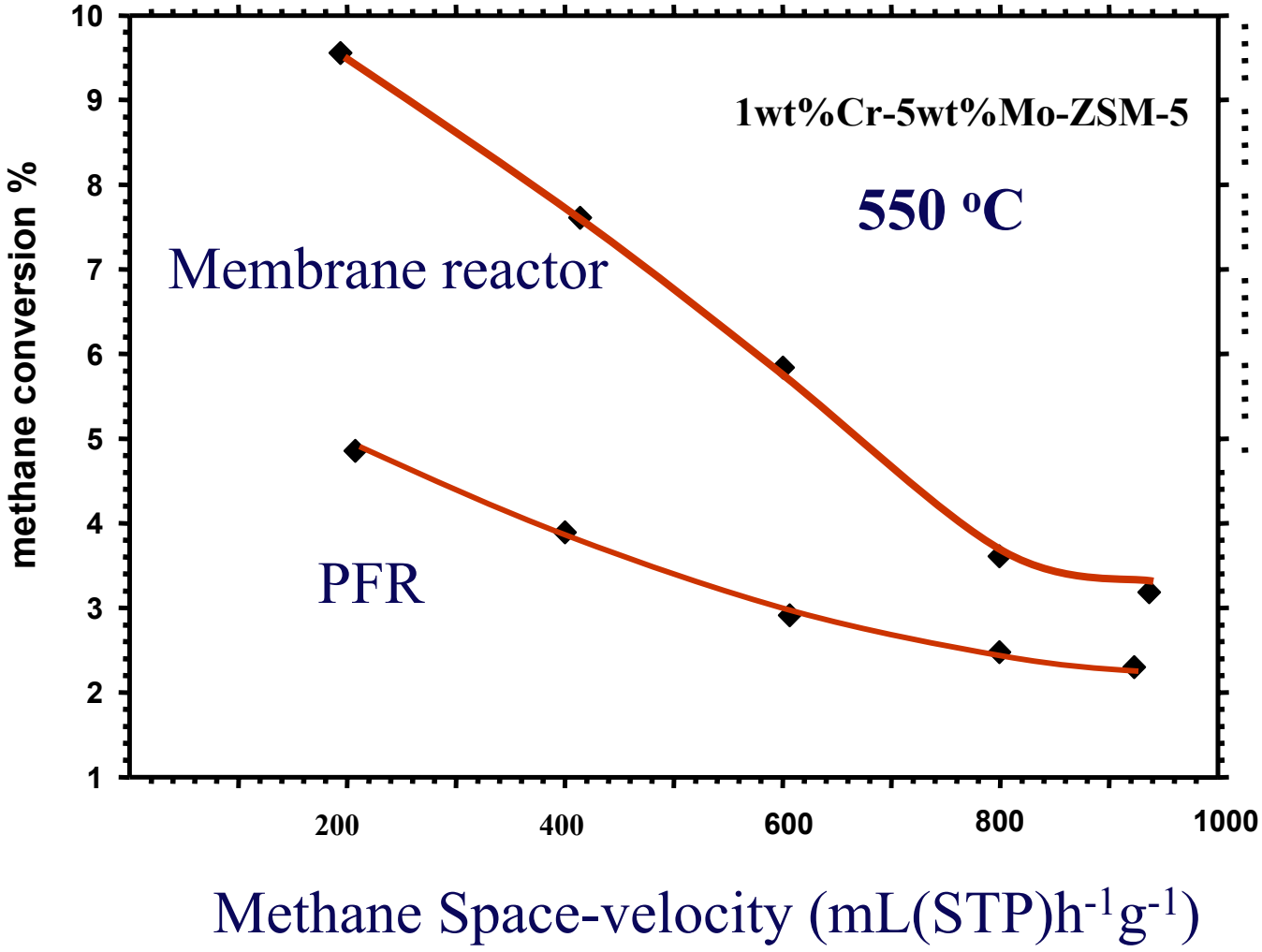


SEM images


0.5wt%Pd-3wt%Mo-ZSM-5
Before reaction
BET S_a=338m²/g
20.0kV x15000 1µm


0.5wt%Pd-3wt%Mo-ZSM-5
After reaction
BET S_a=214m²/g
20.0kV x15000 1µm

Methane Conversion vs. Space Velocity



Future Plans

- Investigate ZSM-5 and H-ZSM-5 zeolite supports → Brönsted-acid sites
- Optimize the parameters of the reaction: lowering the reaction T, P and Space Velocity (recycle)
- Study the kinetics of the reaction and model the membrane reactor and reaction rate → Scale-up
- Reduce coking through recycle and non-equilibrium pulsed discharge.

Publications & Patents

A. Kababji, B.A Grayson, J. T. Wolan, E.K. Stefanakos, and B. Krakow, ***"Synthesis and Characterization of Ru-Mo/HZSM-5 Catalyst ,"*** submitted to Cat. Today August, 2005

A. Kabobji, L.K. Stefanakos, and J.T. Wolan, ***"Design and Development of a nonceramic selectively permeable membrane Reactor"***, *submitted to J. Appl. Catalysis, July 2005.*

A. Kabobji, L.K. Stefanakos, and J.T. Wolan***, "Low Temperature Catalytic Oxygen-free Hydrogen Production via a Novel Membrane Reactor,"*** *submitted to Catalysis Today, August 2005.*

A. Kababji, J. T. Wolan,and K. Stefanakos

Catalysts for hydrogen and benzene production via methane non-oxidative aromatization, **Oral talk accepted for Spring AIChE meeting in Cincinnati, Ohio, November, 2005**

J.T. Wolan, A, Upadhyay, and K. Stefanakos**,** ***"Novel Partial Oxidation of Methane via Electrocatalytic Reactions,"*** presented at the AVS Florida Chapter Conference, 2003, March 8-12

A. Gopalkrishna, J.T. Wolan and S.E Saddow, ***"Catalytic Study of Methane Oxidation,"*** USF Master's Thesis, May, 2003

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